

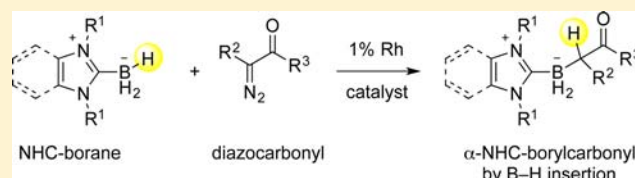
Insertion of Reactive Rhodium Carbenes into Boron–Hydrogen Bonds of Stable N-Heterocyclic Carbene Boranes

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S Supporting Information

ABSTRACT: Readily available rhodium(II) salts catalyze reactions between NHC-boranes (NHC-BH₃) and diazocarbonyl compounds (N₂CRCOR'). Stable α -NHC-boryl carbonyl compounds (NHC-BH₂-CHRCOR') are isolated in good yields. The reaction is a reliable way to make boron–carbon bonds with good tolerance for variation in both the NHC-borane and diazocarbonyl components. It presumably occurs by insertion of a transient rhodium carbene into a boron–hydrogen bond of the NHC-borane. Competitive experiments show that a typical NHC-borane is highly reactive toward rhodium carbenes.



INTRODUCTION

N-heterocyclic carbene-boranes (NHC-boranes) differ in fundamental respects from other classes of borane-Lewis base complexes.¹ Complexes of the parent borane (NHC-BH₃) are remarkably robust. They are typically white solids that are stable to air and water, strong base, and mild acid. They resist dissociation to release reactive BH₃ even under relatively forcing conditions.

NHC-boranes with additional boron-substituents (NHC-BH₂R, NHC-BHR¹R²) can be made by direct complexation of NHCs with substituted boranes whenever the needed boranes (BH₂R, BHR¹R²) can be accessed by hydroboration or other means (Figure 1a, left side).² But when R is functionalized, the complexation route is often not practical because trivalent

boranes are Lewis acids that are not compatible with many functional groups.

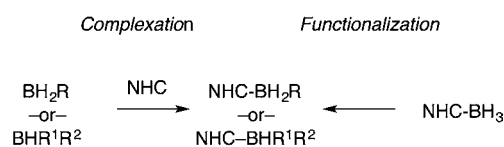
Various functionalized NHC-boranes can be made from the parent NHC-BH₃ complexes (Figure 1a, right side) by direct substitution reactions with electrophiles and by reactions of appropriately activated NHC-boranes with nucleophiles.³ Reactions of NHC-boryl radicals,⁴ and boryl anions⁵ also offer opportunities to make functionalized NHC-boranes, as do hydroboration reactions catalyzed by borenium ions or metals.⁶

Recently, we became interested in studying unknown α -NHC-boryl carbonyl compounds, NHC-BHRCH₂COR'.⁷ These might rearrange by 1,3-boryl shift to boron enolates⁸ or behave as nucleophiles themselves. They can also be considered as unusual analogs of protonated α -amino ketones, acids, and esters (⁺NH₃CHRCOR') where a tetravalent atom with a negative formal charge (B) replaces one with a positive formal charge (N).⁹ NHC-boranes are good hydride donors,¹⁰ so we hypothesized that they would also be good carbenophiles, reacting especially with transient electrophilic¹¹ carbenes (:CHRCOR') or metal carbenes (MCHRCOR') by direct B–H insertion (Figure 1b).

Insertions into hydrogen-element bonds are defining reactions of transient carbenes.¹² Although bimolecular reactions of carbenes and metal carbenes with C–H bonds often occur with low selectivities and low yields, intramolecular insertions are high value synthetic transformations.¹³ In addition, Davies has discovered that selective bimolecular insertions into activated C–H bonds are often possible with rhodium carbenes bearing one acceptor and one donor (typically aryl or alkenyl) substituent.¹⁴

In contrast, the literature on reactions of boron–hydrogen bonds with carbenes is sparse. Carboethoxycarbene (generated by irradiation of ethyl diazoacetate) inserts into the B–H bond

(a) Routes to B-functionalized NHC-boranes



(b) Proposed carbene insertion reactions



Figure 1. (a) B-functionalized NHC-boranes are made by complexation of trivalent boranes or by functionalization of parent NHC-boranes and (b) proposed B–H insertion reactions of carbenes or metal carbenes (M = metal) to make α -NHC-boryl carbonyl compounds.

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of an *o*-carborane in low yield,¹⁵ while Fisher alkynylcarbene complexes react with NaCNBH₃ by insertion.¹⁶ And dichlorocarbene (generated by α -elimination reactions) inserts into B–H bonds of amine- and phosphine-boranes.¹⁷ However, the resulting products L–BH₂CHCl₂ (L = amine or phosphine) are subject to decomplexation and internal redox reactions and are not especially stable. The samarium carbenes derived from CH₂I₂ and CH₃CHI₂ insert into B–H bonds of phosphine-boranes although P–H insertions are faster.¹⁸ A recurring theme in this reactive carbene chemistry is the use of large excesses (7–40 equiv) of carbene-generating reagents.^{17,18}

Here we report that rhodium-catalyzed reactions of diazocarbonyl compounds,^{13,14,19} with readily available NHC-boranes give rise to diverse α -NHC-boryl carbonyl compounds. These transformations presumably occur by B–H insertion reactions of transient rhodium carbenes, and the B–H bonds are far more reactive than common activated C–H bonds. The α -NHC-boryl carbonyl products are stable, and so far they have exhibited no tendency to rearrange to NHC-boryl enolates.

RESULTS AND DISCUSSION

Survey of Reaction Conditions. Table 1 shows key test reactions of readily available 1,3-dimethylimidazol-2-ylidene

Table 1. Results of Representative Initial Experiments with NHC-Borane 1 and Ethyl Diazooacetate 2a

entry	equiv 2a	catalyst (%)	conv (%) ^a	yield 3a (%) ^b	yield 4a (%) ^a
1	1.2	Rh ₂ (OAc) ₄	94	62	14
2	1.2	Rh ₂ (esp) ₂	92	62	12
3	0.8	Rh ₂ (OAc) ₄	75	53	7
4	3.0	Rh ₂ (OAc) ₄	96	40	22

^aEstimated from the ¹¹B NMR spectrum of the crude product;

^bIsolated by automated flash chromatography.

borane 1 and ethyl 2-diazoacetate 2a with two common catalysts for C–H insertions: (1) dirhodium tetraacetate²⁰ [Rh₂(OAc)₄], and (2) dirhodium bis-3,3'-(1,3-phenylene)-bis(2,2-dimethylpropanoate) [Rh₂(esp)₂].²¹ In a typical experiment, a slight excess of diazoacetate 2a (1.2 equiv) was added by syringe pump over 4 h to a solution of NHC-borane 1 (1 equiv) and Rh₂(OAc)₄ (1 mol %) in dichloromethane at 40 °C (entry 1). The ¹¹B NMR spectrum of the crude product showed a large triplet –28.3 ppm, which we assigned to the insertion product 3a. There was also a smaller doublet at –20.3 ppm, which we assigned to the double insertion product 4a, along with an even smaller quartet from remaining 1 (–37.5 ppm, 6%).

Purification of the crude product by flash chromatography with 1/1 hexane/ethyl acetate provided pure insertion product 3a in 62% yield. (All reported yields are based on the NHC-

borane component and are not corrected for recovered starting material unless indicated.) That 3a is an α -NHC-boryl acetate (C–B bond) and not an NHC-boryl enol (O–B bond) was clear from the chemical shifts in the NMR spectra. The resonances for the CH₂ group adjacent to boron were shielded in both the ¹H (1.62 ppm, broad) and ¹³C (24.4 ppm, q, J_{CB} = 32 Hz) NMR spectra. And the ester carbonyl carbon of 3a resonated at 181.1 ppm in ¹³C NMR spectrum.

In contrast to the convenient isolation of monoinsertion product 3a, the very polar double insertion product 4a did not emerge from the column even when 100% ethyl acetate was used as eluent.²² Its yield was estimated at 14% based on the ¹¹B NMR spectrum of the crude product. A similar reaction with the more reactive Rh₂(esp)₂ catalyst (entry 2) gave generally similar results to Rh₂(OAc)₄. Here the target product 3a was also isolated in 62% yield and the estimated yield of 4a was 12%.

Next we varied the amount of diazoester 2a while keeping the catalyst as Rh₂(OAc)₄. A reaction with a slight deficiency of ethyl diazoacetate 2a (0.8 equiv) gave 53% monoinsertion product 3a and 7% di-insertion product 4a along with 25% recovered 1 (entry 3). With excess 2a (3 equiv, entry 4), there was less 3a (40%), more 4a (22%), and only a trace of unreacted 1 (4%).

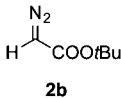
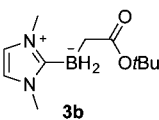
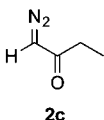
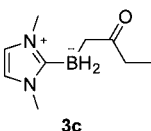
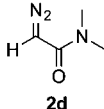
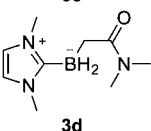
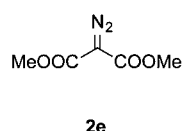
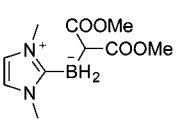
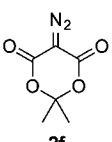
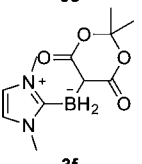
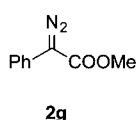
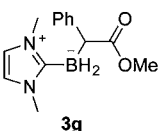
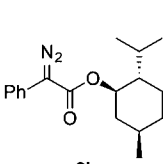
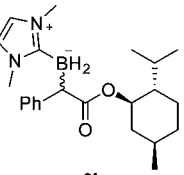
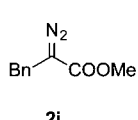
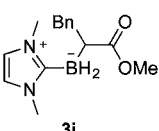
Scope Studies: Diazo Partner. On the basis of the results in Table 1 along with other test reactions (see Supporting Information), we settled on the use of 1.2 equiv of diazo partner to test the scope of the reactions of 1 with various diazocarbonyl compounds. The results of representative reactions in this series are summarized in Table 2. The catalyst Rh₂(esp)₂ typically gave similar or better yields compared to Rh₂(OAc)₂, so only the Rh₂(esp)₂ results are shown.

tert-Butyl diazoacetate 2b, 1-diazobutan-2-one 2c, and 2-diazo-*N,N*-dimethylacetamide 2d all gave similar results to ethyl diazoacetate 2a (compare Table 2, entries 1–3 with Table 1, entry 2). Conversions of 1 ranged from 66–80%, and isolated yields of stable insertion products 3b–d were 58%, 49%, and 55%, respectively. As with substrate 2a, small amounts of double insertion products were formed in these experiments (estimated 11%, 10% and 19% by ¹¹B NMR spectroscopy), but these products were not isolated. Instead, we targeted several unsymmetrical double insertion products (see Scheme 1 below).

Diazoesters bearing additional conjugating substituents gave better conversions and yields.²³ Dimethyl diazomalonate 2e produced α -NHC-boryl malonate 3e in 73% yield (entry 4), while diazodimedone 2f provided 3f in 60% yield (entry 5). The Davies-type¹⁴ donor–acceptor precursor methyl 2-phenyldiazoacetate 2g gave 3g in 74% yield (entry 6). Reaction of 1 with (–)-menthyl diazoacetate 2h and the standard Rh₂(esp)₂ catalyst provide 3h as an 81/19 mixture of diastereomers in 60% yield (entry 7). We have not yet succeeded in separating these diastereomers, so their configurations are unassigned.

In contrast to the successes with additional conjugating substituents, methyl 2-benzoyldiazoacetate 2i²⁴ gave 3i in only 26% yield (entry 8). The main problem here is not the formation of di-insertion product but the low conversion; the yield of 3i based on recovered starting material is actually 93% because only 28% of 1 was consumed. A similar result was obtained in a reaction of 1 and 2i conducted at 84 °C in 1,2-dichloroethane while no product was formed in acetonitrile (see Supporting Information, SI).

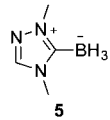
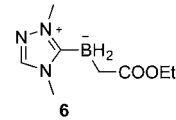
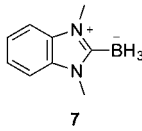
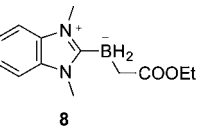
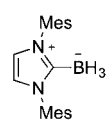
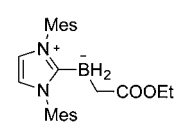
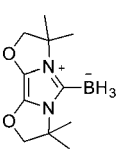
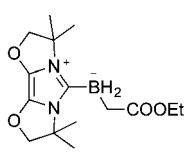
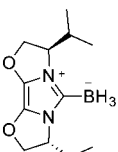
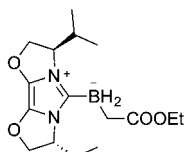
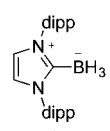
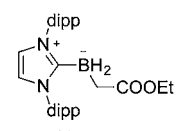
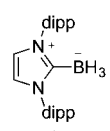
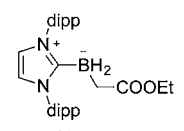
Table 2. Scope of the B–H Insertion with 1% Rh₂(esp)₂: Variation of the Diazo Partner^a

entry	diazo partner	product	conv.	yield
1			71%	58%
2			66%	49%
3			80%	55%
4			96%	73%
5			83%	60%
6			98%	74%
7			61%	60% ^b
8			28%	26%

^aSame conditions as Table 1 entry 2. ^b81/19 mixture of diastereomers.

Scopes Studies: NHC-Borane Partner. We selected NHC-borane **1** for the initial survey in part because it offered little opportunity for competing bimolecular reactions of the rhodium carbenes with the NHC ring or its substituents. We next varied the structure of the NHC-carbene partner while holding the diazo partner as ethyl diazoacetate **2a**. The standard conditions were used with the Rh₂(esp)₂ catalyst, and the results are summarized in Table 3. Results with triazolylidene borane **5**, benzimidazolylidene borane **7** were similar to dimethylimidazolylidene borane **1**. Conversions were 65–80% and isolated yields of monoinsertion products **6** and **8** were 52% and 60% (entries 1, 2). Minor amounts of di-insertion products were formed (11% estimated yield from **5** and 19% isolated yield from **7**, see SI).

Table 3. Scope of the B–H Insertion with 1% Rh₂(esp)₂: Variation of the NHC-Borane Partner^a

entry	NHC-BH ₃	product	conv.	yield
1			72%	52%
2			80%	60%
3			65%	60%
4			66%	60%
5			66%	59%
6a			65%	63%
6b			100%	96%

^aSame conditions as Table 1, entry 2 with 1.2 equiv of diazoester **2a**.
^b3 equiv of diazoester **2a**

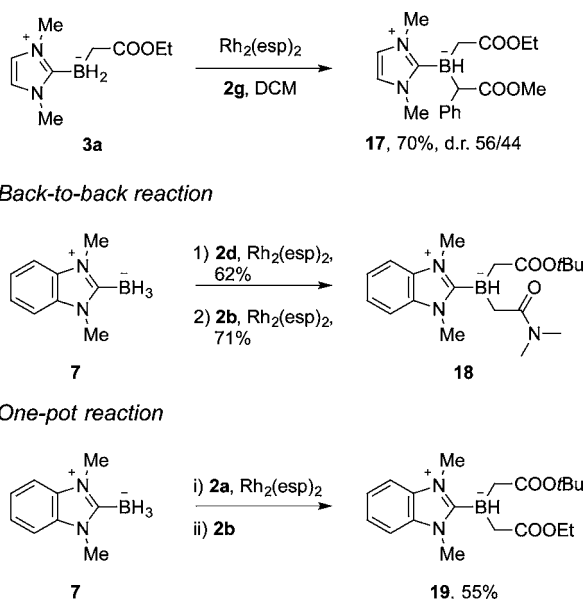
With bulkier substrates dimesitylimidazolylidene borane **9**, tricyclic boranes **11** and **13** (enantiopure), and dipp-imidazolylidene borane **15** (dipp is 2,6-diisopropylphenyl), the conversions of NHC-boranes were a bit lower but there was not much double insertion product formed (entries 4–6a). Indeed, the isolated yields of monoinsertion products **10**, **12**, **14** (enantiopure), and **16** (59–63%) approached the conversions of the precursors (65–66%). In the first three cases (**9**, **11**, **13**), only 5–6% of the di-insertion product was detected. And in the case of the very hindered dipp borane **15**, there was no resonance at all for the di-insertion product in the ¹¹B NMR spectrum of the crude product (entry 6a).

These results suggest that the only significant competing pathway for B–H insertion to **15** is reaction of the rhodium carbene with itself or its precursor. This in turn suggests that higher yields might be obtained by increasing the amount of the diazo precursor. This approach failed with the smaller NHC-borane **1** because the di-insertion product was formed competitively (see Table 1, entry 4). In contrast, a reaction

of dipp-Imd-BH₃ **15** with 3 equiv of ethyl diazoacetate **2a** gave complete conversion of **15**, and isolated yield of insertion product **16** increased from 63% (entry 6a) to 96% (entry 6b).

Unsymmetrical Double Insertion Products. We also briefly investigated the formation of unsymmetrical double insertion products by treatment of the monoinsertion products from one diazo compound with a second, different diazo compound, as shown in Scheme 1. Reaction of insertion product **3a** with methyl 2-phenyldiazoacetate **2g** (2 equiv) provided separable diastereomers of the double insertion product **17** in 70% combined yield (56/44 diastereomer ratio). These diastereomers arise because the boron atom and one of the adjacent carbon atoms in **17** are both stereogenic centers. The phenyl substituent in this product is important for purification since related diesters lacking it (for example, **4a**) did not reliably come off the column.

Scheme 1. Stepwise and One-Pot Formation of Double Insertion Products



Back-to-back reaction of benzimidazolylidene borane **7** with two different diazo compounds gave a chiral product **18** whose only stereocenter is at boron. A first reaction with diazoamide **2d** and Rh₂(esp)₂ was followed by a second, similar reaction with *tert*-butyl diazoacetate **2b** and the same catalyst to give **18**. The yield of the first insertion was 62% while the second insertion occurred in 71% yield.

The two enantiomers of **18** were stable on both silica gel and on an (*S,S*)-Whelk-O1 column with a chiral stationary phase. A small amount of the racemate (22 mg) was preparatively resolved on the chiral column to give about 10 mg each of the two component enantiomers in high enantiopurity. Optical rotations were -34 (first eluting enantiomer) and $+33.8$ (both $c = 1$, CHCl₃). To the best of our knowledge, this is the first example of isolation and characterization of stable enantiomers of a chiral carbene-borane whose only stereocenter is on boron.

Finally, a sequential one-pot reaction at 40 °C was also successful. First, ethyl diazoacetate **2a** (1.2 equiv) was added by syringe pump over 4 h to benzimidazolylidene borane **7** (1 equiv) and 1% Rh₂(esp)₂. Like some of the other reactions (see SI), the color of the mixture gradually changed from green to orange.²¹ Just as the first syringe pump stopped, a second was

started and *t*-butyl diazoacetate **2b** (2 equiv) was added, again over 4 h. Although the mixture remained orange, TLC analysis showed that the second insertion was progressing during the second syringe pump period. Standard workup and chromatography gave diester **19** in 55% isolated yield.

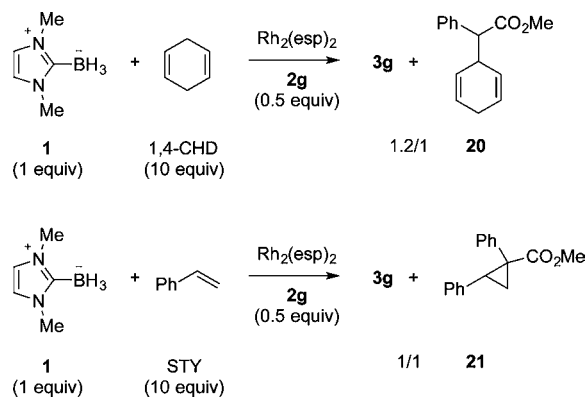
Competitive Rate Experiments. The NHC-rings and *N*-substituents of the precursors in Table 3 and Scheme 1 contain various potential sites for reactions of rhodium carbenes, including aromatic rings and activated C–H bonds. However, side products from reaction at sites other than boron have so far not been isolated. This implies that the B–H bonds of these NHC-boranes are very reactive toward rhodium carbenes. This notion is also supported by the good yields obtained without large excesses of reagents and by the scope of the different diazo compounds that can be used.

To better address the reactivity question, we tapped into a scale put forth by Davies and co-workers.²⁵ The scale is for reactions between various carbenophiles and methyl 2-phenyldiazoacetate **2g** catalyzed by Rh₂(S-DOSP)₄ (DOSP is 4-dodecabenzenesulfonyl proline). We used the Rh₂(esp)₂ catalyst for internal consistency, so we cannot place our results quantitatively on the Davies scale. Still, the key conclusion—that boron–hydrogen bonds are highly reactive carbenophiles—is clear-cut.

We started competition experiments with **1** and THF, whose CH₂O groups are considered to be activated toward C–H insertion of Rh-carbenes.²⁵ But in the preliminary reactions of **2g**, **1** and THF, the THF insertion product was hardly formed at all even when THF was used in 50-fold excess over **1**. The THF did not interfere with the B–H insertion reaction, and **3g** was the major product as usual.

We then moved directly to the top of the Davies reactivity scale with 1,4-cyclohexadiene and styrene (Scheme 2).

Scheme 2. Competition Experiments of NHC-Borane 1 with 1,4-Cyclohexadiene (1,4-CHD) and Styrene (STY)



Competition of 1 equiv of 1,4-cyclohexadiene (1,4-CHD) and 1 equiv **1** again provided **3g**, this time with a little of the cyclohexadiene C–H insertion product. Finally, competition of a 10-fold excess of 1,4-CHD with **1** provided the B–H insertion product **3g** and the C–H insertion product **20** in a ratio of about 1.2/1.

Likewise, reaction of **1** and styrene (STY) in a 1/1 ratio gave **3g** with only a small amount of the styrene cyclopropanation product. However, competition of 1 equiv of **1** with 10 equiv of styrene gave **3g** and **21** in about a 1/1 ratio.

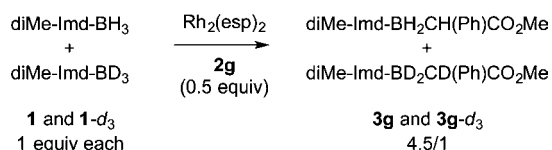
These results show that NHC-borane **1** is roughly 10–12 times more reactive than 1,4-cyclohexadiene and styrene, and it

is over 100 times more reactive than THF. Accordingly, the B–H bonds in **1** are much more reactive than typical “activated” C–H bonds toward rhodium carbenes. Further, a better comparable compound to NHC–BH₃ would contain a CH₃ group rather than a CH₂ group. However, methyl groups rarely participate in selective bimolecular insertion reactions.^{13,14} Clearly, NHC-boranes are potent carbenophiles toward electrophilic rhodium carbenes and, by extension, other classes of electrophilic carbenes or metal carbenes.

Isotope Effect Experiments. Finally, we conducted simple experiments to estimate the bimolecular isotope effect in a typical B–H insertion reactions. Here again, comparables are provided by Davies in Rh₂(S-DOSP)₄-catalyzed reactions of labeled and unlabeled substrates with methyl 2-phenyldiazoacetate **2g**. The isotope effect was about 2 in a competition of cyclohexane with cyclohexane-*d*₁₂ and about 3 with THF and THF-*d*₈.²⁵

The key competition experiment in the NHC-borane series required care because a control experiment with **1** (diMe-Imd-BH₃), **1-d**₃ (diMe-Imd-BD₃, >95% D) and Rh₂(esp)₂ but lacking the diazoester showed that H/D exchange occurred over some hours at 40 °C. No exchange occurred without the catalyst. The exchange was easy to follow approximately by ¹¹B NMR spectroscopy because the multiplicities changed due to the differences in spin and coupling constant (*J*) between H and D; however, it was hard to quantitate accurately because of overlapping. We suspect that the catalyst and the NHC-borane react, perhaps by direct hydride transfer, to make a small amount of a borenium ion (NHC–BH₂⁺) or its reactive equivalent.²⁶ This could catalyze the H/D exchange by reversible hydride/deuteride transfer.^{6a}

Scheme 3. Competition Experiment to Estimate the Isotope Effect



We discovered that the H/D exchange could be superseded at rt by rapidly adding a solution of 0.5 equiv of the methyl 2-phenyldiazoacetate **2g** to a CD₂Cl₂ solution of the catalyst and 1 equiv each of **1** and **1-d**₃. The expected insertion products **3g** and **3g-d**₃ were formed after 5 min in a ratio of about 4.5/1. The unreacted boranes at this point were mostly (>90%) **1** and **1-d**₃, and the exchanged products **1-d**₁ or **1-d**₂ were not prevalent in the ¹¹B NMR spectrum (<10%).

Mechanism. All these data combine to form a consistent picture of the B–H insertion reactions of rhodium carbenes, and Figure 2 shows a simple transition state model. The rhodium-carbene C–H insertion reactions are thought to be concerted but not synchronous,^{13,14} so the B–H insertions may be likewise. In the transition state, the hydride abstraction by the rhodium carbene to form the new C–H bond is advanced (evidenced by the large isotope effect) while the accompanying C–B bond formation lags. In this view, it is productive to model the transition state as having the character of an NHC-borenium ion associated to a rhodium enolate. As the transition state is passed, these two components collapse by *B*-alkylation to form the product and return the catalyst.

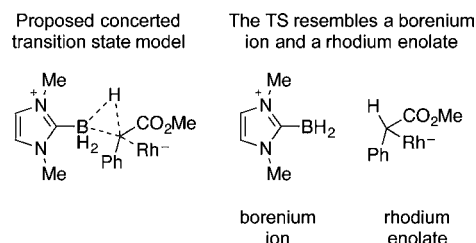


Figure 2. The B–H insertion reaction is probably concerted. The TS shares characteristics of a borenium ion and a rhodium-enolate because hydride abstraction is leading and C–B bond formation is lagging.

NHC-boranes are excellent hydride donors,¹⁰ and have relatively weak B–H bonds (<85 kcal/mol).²⁷ These electronic effects explain why they are such reactive carbenophiles toward electrophilic rhodium carbenes. However, steric effects must also be important because the second insertion to NHC–BH₂R is slower than the first to NHC–BH₃, especially when the NHC ring has large N-substituents.

CONCLUSIONS

Readily available rhodium(II) salts catalyze reactions between NHC-boranes and diazocarbonyl compounds. Stable α -NHC-boryl carbonyl compounds are isolated in good yields, so the reaction is a reliable way to make boron–carbon bonds. There is broad tolerance for variation in both the NHC-borane and diazo carbonyl component. More hindered NHC-boranes actually give better yields of monoinsertion products because the primary products are not subject to a competing second insertion.

These first reactions of stable carbene-boranes with transient metal carbenes suggest that NHC-boranes are superb carbenophiles and encourage further study of their reactions with rhodium carbenes and with other types of metal carbenes.

ASSOCIATED CONTENT

Supporting Information

Experimental details, compound characterization data, and copies of spectra of all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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